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Seaweed biomass of the Philippines: Sustainable feedstock for biogas production

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ABSTRACT

Archipelagic and island countries are among the most affected by the worsening climate change. To mitigate global warming, the Philippines mandated the use of biofuel through the Biofuel Act of 2006. However, coping with the increasing biomass demand for biofuel production is challenging because of the country's limited freshwater and land resources. On the other hand, the Philippines has rich but untapped marine biomass resources. Hence, the potential of seaweed resources as the most accessible energy source for coastal and island communities of the Philippines was explored for methane fermentation. The seaweed species, *Sargassum* spp., *Turbinaria* spp., *Hydroclathrus* spp., *Caulerpa* spp., and *Ulva* spp., which can allow sustainable biomass supply either through managed harvesting of natural stocks or through cultivation, have been identified. Information on the geographical distribution and seasonal productivity of these species were laid out. The proximate and elemental components of the biomass were presented for viability assessment as feedstock. Challenges on biogas technology in the Philippines and anaerobic digestion of seaweed biomass were also evaluated. Research on the development of culture technologies for the *Sargassum* spp., *Turbinaria* spp., *Hydroclathrus* spp, and *Ulva* spp. is recommended to avoid the adverse impacts of harvesting on natural stocks. Further studies on anaerobic digestion conditions of the selected seaweeds that are suitable for utilization by island communities should also be conducted.

Contents

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1. Introduction

Oil crisis in the 1970s drove the development of biogas technology [1] using several species of macroalgae [2,3] as one of the renewable energy solutions. Interest in renewable energy waned when oil prices stabilized because of the discovery of new oil fields. Recently, the interests in marine biomass utilization for biofuel production reemerged due to several reasons. These are (1) mitigation of climate change by lowering CO_2 emissions, and maintaining the closed carbon cycle [4], (2) energy security by decreasing the reliance on petroleum fuels, and its erratic price fluctuation [5], (3) food security by avoiding the indirect and direct competition on terrestrial food crops utilization for biofuel production, and preventing high food prices [6], (4) better feedstock compared to terrestrial crops by having faster growth rate [7], and (5) environmental conservation and preservation by preventing forest conversion to biofuel crop farms [8].

The Philippines is among the most impacted countries of global warming as shown on its global risk index rank – from third place in 2009 [9] to second place in 2012 [10]. To mitigate climate change and its inevitable risks and impacts, the Philippine government institutionalized the Biofuel Act of 2006 (Republic Act 9367), which mandates the blending of gasoline with bioethanol from 10% in 2012 to 20% in 2025 and of diesel with biodiesel from 2% in 2012 to 10% in 2025 [11]. The Energy Regulatory Commission also approved a feed-in-tariff of Php6.63/kWh (~US$0.15) for electricity generated from biomass renewable energy last July 2012 [12]. The support from the different sectors in rapidly developing the bioethanol and biodiesel industries helps in achieving the clean energy goals of the Philippines. Nevertheless, whether or not these efforts are sustainable in the long term is still uncertain.

Biodiesel and bioethanol are liquid biofuels that are preferred commercially because these are easy to transport and can be readily mixed with petroleum gasoline and diesel [13]. Coconut oil supplies most of the biodiesel demand in the Philippines, but other feedstock such as *Jatropha* and palm oil are also explored [14]. On the other hand, bioethanol production heavily relies on sugarcane, but it can only supply 79% of the country's need [14]. The demand for bioethanol production may continue to increase with the encouragement of the Philippine government on biofuel use. However, the sustainability of these mechanisms remains uncertain. The conversion of arable and traditional food crop-producing farms to biofuel feedstock production may negatively affect food security, considering the steady growth of the Philippine population. Decrease in food crop production may also increase the price of food, reducing the accessibility of the masses. Moreover, large-scale mono-cropping for biofuel feedstock may have negative environmental effects such as biodiversity loss, which is in conflict with various national policies and mechanisms on environmental conservation and protection. These factors can pose a problem in achieving the country's goal on biofuel sustainability.

Among the biomass-utilizing biofuel technologies (e.g., bioethanol fermentation and biodiesel production), biogas production is the most efficient in terms of net energy gain [15] because anaerobic digestion utilizes all the degradable components (carbohydrate, protein and lipid) of the feedstock [16] to produce biogas (~60% CH_4, ~40% CO_2 and other trace gases). Biogas can also be upgraded to increase its methane content up to the same level as that of natural gas, giving the same performance when used as fuel in internal combustion engines or as household cooking gas. The limited land resources of the Philippines for biomass cultivation made biogas technology important to its long term green energy goal because of the wider range of crops suitable for biogas production, as compared to biodiesel and bioethanol.

The archipelagic nature of the Philippines isolates many islands and coastal communities, resulting in the limited access of these areas to a centralized power source. Despite the government's increased efforts to provide electricity for its people, many distant and poor communities still have insufficient, if not complete absence of, electricity supply. The use of household biogas digesters for the production of biogas as an alternative and climate-friendly fuel source may be suitable and practical, especially for poor families residing in these many and widespread isolated communities.

The Philippines' coastline is 36,289 km long – the second longest in Asia and the fourth in the world [17]. However, the country's abundant marine resources, especially the often conspicuous seaweed resources, remain relatively unexplored and underdeveloped for the sustainable production of biofuel feedstock. Seaweeds have long been part of the lives of coastal communities in the Philippines. Seaweeds can be categorized on the basis of its use, namely, as food, source of phycocolloids, and source of other natural products used in various applications [18]. Out of the 350 species (820 species listed for the country) that have known economic values, less than 5% are commercially important. Among these commercially important species, only the phycocolloid-producing species, the agarophytes (*Gracilaria* spp. and *Gelidiella acerosa*) and the carrageenophytes (*Eucheuma* spp. and *Kappaphycus* spp.), gained considerable attention. The potential of other seaweed resources of the country remains untapped, and the majority remains underdeveloped or undeveloped [18].

Although seaweed resource utilization in the Philippines is mostly focused on natural product extraction, the increasing interest in the utilization of these biomasses for biofuel, specifically biogas production, instigated this review. Hence, this study aimed to determine the different seaweed species in the Philippines that can be sustainably utilized as biogas feedstock for commercial or household use. The biomass productivity, as

well as composition and degradability of the seaweeds are also discussed. Research on the anaerobic digestion of marine biomass suitable for utilization by coastal and island folks is presented.

2. Seaweed biomass: prospects for sustainable feedstock

The criteria for the selection of species for biofuel production generally include the following: (1) the species must be available in large quantities in many areas of the country, that is, it should sustainably provide for the requirements of production; (2) the species should be available year round or in most part of the year; and, (3) sustainable cropping (or cultivation) can be conducted without adverse effects on the environment. Several species satisfy at least one, if not all, of these criteria. These species are the brown seaweeds *Sargassum* spp., *Turbinaria* spp., and *Hydroclathrus* spp. and the green seaweeds *Caulerpa* spp. and *Ulva* spp. (Fig. 1). Although members of the genus *Eucheuma*, *Kappaphycus*, *Gracilaria* and *Gelidiella* may also satisfy these criteria, these seaweeds are more economically valuable as feedstock for the production of natural products than for biofuel production.

2.1. The genus Sargassum

The members of the genus *Sargassum* C. Agardh (Phylum Ochrophyta, Class Phaeophyceae, Order Fucales, and Family Sargassaceae) are widely distributed and common in the Indo-Pacific region. Currently, this genus has 335 taxonomically accepted species [20]. At least 29 of the more than 90 species reported in the Philippines have been validated. Members of this genus are conspicuous and form extensive beds along the rocky shores of the country.

In addition to its high ecological value, *Sargassum* is well known for its economically important natural products such as alginates, fucoidan, fucoxanthin, and lutein. The ethnobotanical uses of *Sargassum* biomass by coastal populations across the country include its use as a cover for the prevention of desiccation and maintenance of freshness of fishery products, food, plant fertilizer and flower inducer, insect repellant, animal feed in agriculture, and therapeutic drink, among others [21]. *Sargassum* biomass also has great potential as feedstock for biofuel [22].

2.1.1. Biomass distribution and production

Sargassum biomass production in the Philippines, as in any part of the world, coincides with the growth and development of the species (i.e., period of regeneration or recruitment, fast growth phase, reproduction, senescence, and die-back) [23–32]. According to various studies conducted in the country, *Sargassum* biomass production is low during recruitment, but increases during the fast growth phase. Biomass production peaks during reproduction, and consequently decreases at the onset of senescence and die-back. During the latter stage, much of the biomass produced are uprooted and washed ashore. These dislodged seaweeds, together with sea grasses (collectively known as sea wrack), can be collected and used for biogas production as demonstrated by Marquez et al. [33]. Moreover, in the absence of technology for the mariculture of *Sargassum*, a cropping management scheme for existing *Sargassum* beds was developed by Trono and Tolentino [34] to maximize the utilization and conservation of the available harvestable biomass from natural beds. Intertidal populations can

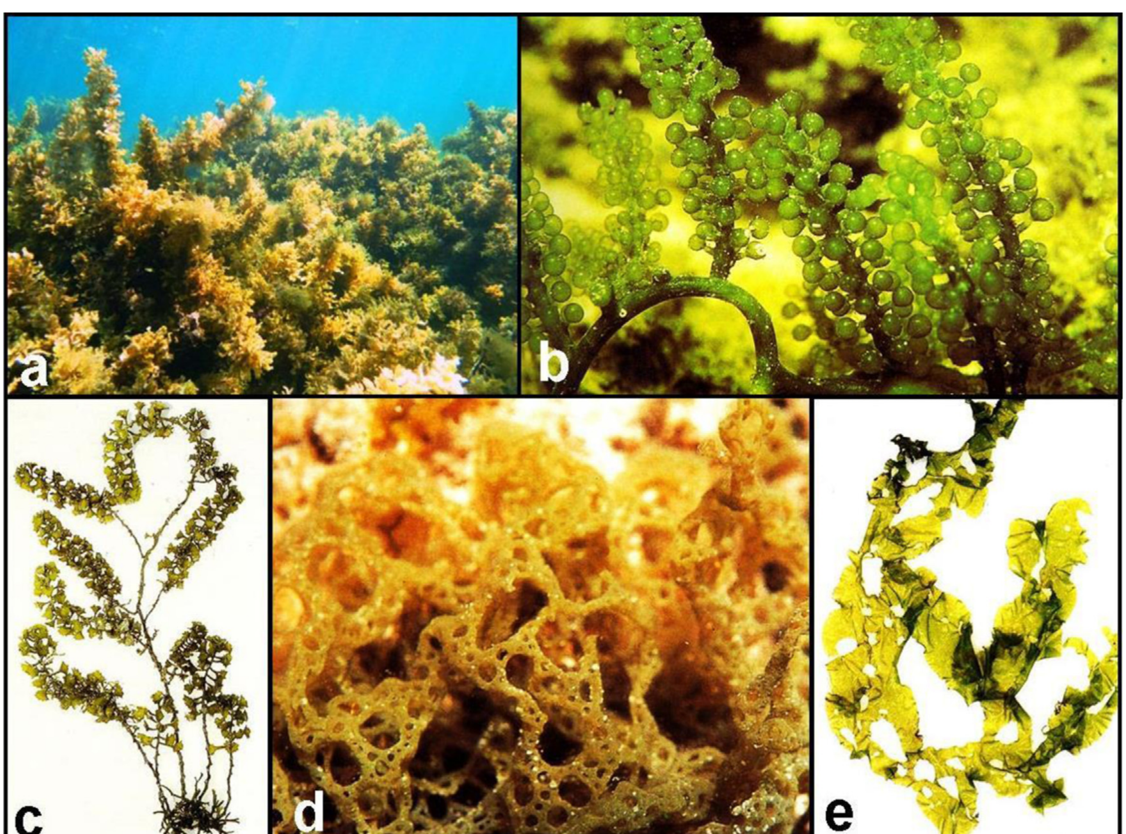

Fig. 1. The seaweed resources of the Philippines ((a) *Sargassum* bed; (b) *Caulerpa lentillifera*; (c) *Turbinaria conoides*; (d) *Hydroclathrus clathratus*; and (e) *Ulva reticulata*) with high potential as feedstock for biogas production. Photo courtesy of (a) WJE Santiañez and (b–e) Trono [19].

be harvested once a year, and subtidal populations can be harvested at least twice. Harvests can be scheduled before fertility peak or when approximately 50% of the populations are fertile. This strategy allows the species to regenerate and proceed to the regular reproductive phase. Moreover, pruning must be conducted near the base, ensuring that both the holdfast and primary laterals are left to avoid interference with the regeneration process [23]. Harvest must also be conducted in strips or randomly to ensure enough fertile materials for recruitment [34].

Studies on *Sargassum* biomass production in the Philippines are summarized in Table 1. Many of the *Sargassum* beds produce high biomass during the last quarter of the year (November to December). Given these information, insights on harnessing the potential of *Sargassum* biomass for biogas production can be derived.

Table 1
Biomass production of *Sargassum* species in the Philippines.

Species	Highest biomass (kg wet weight/m^2)	Period	Locality	Ref.
S. binderi	3.36		Mactan Is., Cebu	[35]
	0.667		Taklong Is., Guimaras	[36]
S. crassifolium	2.55	August	Maydolong, Samar	[37]
	13.19	January/February	Calarian, Zamboanga	[38]
	2.98	January/February	Bolinao, Pangasinan	
	0.647	December	Bolinao, Pangasinan	[39]
S. cristaefolium	0.430	November	Bolinao, Pangasinan	
	0.242	September	Ilocos Sur	[40]
	0.111[a]	February	Negros Island	[26]
S. feldmanii	0.723[a]	March	Negros Island	
S. hemiphyllum	0.963	March	Maydolong, Samar	[37]
S. ilicifolium	0.124[a]	February	Negros Island	[26]
	15.60	January/February	Calarian, Zamboanga	[38]
	2.38	October	Maydolong, Samar	[37]
S. oligocystum	0.282	November	Bolinao, Pangasinan	[39]
	1.60	December	Maydolong, Samar	[37]
S. polycystum	0.011[a]	May	Negros Island	[26]
	0.447	December	Bolinao, Pangasinan	[39]
	3.07	July	Liloan, Cebu	[41]
	11.09	January/February	Quezon, Palawan	[38]
	12.08	January/February	Aborlan, Palawan	
	3.51	December	Maydolong, Samar	[37]
	1.24	August	Pasacao, Camarines Sur	[42]
	4.30		Danajon Reef, Bohol	[43]
S. siliquosum	6.61	December	Liloan, Cebu	[41]
	11.36	January/February	Aborlan, Palawan	[35]
	2.69		Mactan Is., Cebu	
	4.89	January	Maydolong, Samar	[37]
Sargassum spp.	0.478[a]	August	Calatagan, Batangas	[44]
	1.08		Calarian, Zamboanga	[35]
	7.16		Aborlan, Palawan	
	4.70		Tadtaran, Quezon	
	4.14		Cidanao, Quezon	
	4.25		Bolinao-Anda, Pangasinan	[43]
	3.20		Currimao, Ilocos Norte	
	8.40		Burgos, Ilocos Norte	
	3.81		Nasugbu Bay, Batangas	
	3.00		Matabungkay, Batangas	
	0.335[a] (intertidal)	March	Currimao, Ilocos Norte	[45]
	0.600[a] (subtidal)	July		

[a] Indicates dry weight values.

Table 2
Biomass production of the seaweed genera *Caulerpa*, *Ulva*, *Hydroclathrus*, and *Turbinaria* in the Philippines.

Species	Highest biomass (kg wet weight/m^2)	Period	Locality	Ref
Chlorophyta				
C. lentillifera	1.53	April–May (pond culture)	Calatagan, Batangas	[51]
U. lactuca	2.60	March	Mactan Is., Cebu	[52]
U. reticulata	0.150	March	Mactan Is., Cebu	
Phaeophyceae				
H. clathratus	0.204	April	Taklong Is., Guimaras	[36]
	0.370	February	Ilocos Sur	[40]
	0.017	April	Pasacao, Camarines Sur	[42]
T. conoides	0.421	October	Taklong Is., Guimaras	[36]
T. ornata	0.291	September	Pasacao, Camarines Sur	[42]
	0.278	October	Taklong Is., Guimaras	[36]
T. luzonensis	0.128	October	Pasacao, Camarines Sur	[42]
	0.116	April	Taklong Is., Guimaras	[36]
Turbinaria sp.	1.34		Mactan Is., Cebu	[35]

2.2. The genus *Turbinaria*

The members of the genus *Turbinaria* Lamoroux (Phylum Ochrophyta, Class Phaeophyceae, Order Fucales and Family Sargassaceae [20]) are generally found attached on rocks or sandy-coralline substrates in reef areas with moderate to strong water movement [46]. This genus has at least 22 species (including forms and varieties) in the world [20], most of which are widely distributed in the tropics. At least 10 species (excluding varieties and forms) can be found in the Philippines [47].

2.2.1. Biomass distribution and production

Turbinaria conoides, *T. ornata*, *T. decurrens* and *T. luzonensis* can be found in many coastal areas in the country. All these species, except the latter, are common in the intertidal and subtidal areas of the coasts. Members of the genus *Turbinaria*, especially *T. conoides*, can form thick, huge colonies in subtidal areas [19]. *Turbinaria* beds are among the most conspicuous marine flora in the country, next to *Sargassum* [48].

Studies on the *Turbinaria* species in the country are very limited. In Pasacao, Camarines Sur, the biomass produced by *T. ornata* and *T. luzonensis* peaks on September (0.45 kg/m^2) and October (0.12 kg/m^2), respectively [42]. *Turbinaria* found in Mactan Island, Cebu has a fresh biomass of 1.34 kg/m^2 [35]. Other pertinent information on the seasonal distribution of the different species across the country can be found in Trono [19].

2.3. The genus *Hydroclathrus*

The members of the genus *Hydroclathrus* Bory de Saint-Vincent (Phylum Ochrophyta, Class Phaeophyceae, Order Ectocarpales and Family Scytosiphonaceae [20]) are common in tropical waters but highly seasonal. Peak in abundance occurs during summer and is marked by the formation of dense mats, covering most of the substrate and other benthic organisms [19,46]. Biomass decreases at the onset of the rainy season, leading to complete absence [19]. *Hydroclathrus* has four known species in the world [20], two of which can be found in the Philippines, namely *Hydroclathrus clathratus* and *H. tenuis* [19].

2.3.1. Biomass distribution and production

Hydroclathrus clathratus and *H. tenuis*, are commonly found on reef flats, sometimes attached to rocks or interspersed among sea grasses. Among these two species, *H. clathratus* is more common and abundant, but both are seasonal. Both species are abundant during the period of warmer waters (summer), in the months of March to May or June [19,49]. San Diego-McGlone et al. [50] noted the bloom of *H. clathratus* in Puerto Galera, linking them to nutrient mediated stress (nutrient enrichment). Despite its extreme seasonality, much of the biomass produced by *Hydroclathrus* spp. is underutilized and hence holds great potential for biogas production. However, the scarcity of information on the field biology and ecology of this seaweed may hamper its optimum utilization. The available information on the biomass production capacity of both species in the country is listed in Table 2. Trono [19] summarized the information on the country-wide seasonality of *H. clathratus* and *H. tenuis*.

2.4. The genus *Caulerpa*

The members of the genus *Caulerpa* Lamoroux (Phylum Chlorophyta, Class Bryopsidophyceae, Order Bryopsidales and Family Caulerpaceae [20]) are widespread, occurring in tropical to subtropical waters [53]. The species are known to thrive in calm, sheltered or moderately exposed areas generally with sandy substratum but can also be found growing on muddy, sandy-coralline, and rocky substrates [46]. At least 24 species of *Caulerpa* can be found in the Philippines, excluding the different varieties of each species [47]. Most species are commercially consumed as human food, especially as seaweed salad [19,54].

2.4.1. Biomass distribution and production

Most species (*Caulerpa cupressoides*, *C. lentillifera*, *C. peltata*, and *C. racemosa*) form colonies or wide mats on sandy, muddy or rocky substrates. Among all the species, *C. lentillifera* is the most favored species for consumption; hence, this species is commercially farmed in ponds and lagoons [19]. The farming technology for the mass culture of *C. lentillifera* that was developed in the 1980s [51] provided greater prospect in the utilization and sustainable production of the species as feedstock for biofuel production. Maximum annual production of *C. lentillifera* grown in a 10,000 m^2 farm at a 0.10 kg/m^2 initial seeding may reach up to 1.53 kg/m^2 wet weight [51]. The temporal and spatial distribution of various *Caulerpa* species was documented by Trono [19,54].

2.5. The genus *Ulva*

The members of the genus *Ulva* Linnaeus (Phylum Chlorophyta, Class Ulvophyceae, Order Ulvales, and Family Ulvaceae [20]) are common in the tropics, but can also be found in the subtropical waters of China. The species are often found in shallow intertidal areas that are intermittently exposed to air during low tide. The species can also be found as epiphytes of other large marine algae such as *Sargassum* or on sea grass blades [46]. A total of 98 species can be found in the world [20], 12 of which are found in the Philippines [47], excluding infraspecific names.

2.5.1. Biomass distribution and production

Most species are characteristic flora of eutrophic waters and considered as pollution indicators [52]. Although it can be found all throughout the year, *Ulva* spp. are more abundant from November to April. However, little is known on the actual amount of biomass produced in the different localities across the country. The only report that quantified the biomass of *Ulva* spp. is that of Largo et al. [52] in Mactan, Cebu, where the species form extensive beds (i.e., "green tide") during summer (March) and has fresh biomass reaching up to 2.6 kg/m^2 (Table 2).

3. Biogas production process

Most studies on biofuel production using marine biomass focused on microalgae for biodiesel [55,56] and macroalgae for bioethanol production [57,58]. Biodiesel and bioethanol are liquid biofuels that are commercially preferred because it can readily and easily utilized by different vehicle and industrial engines for power generation. Although biogas can be directly used with gas stoves in households as a substitute for liquefied petroleum gas, it needs further upgrading for commercial engine usage. Therefore, biogas is preferred as a renewable source of energy in rural communities [59,60]. Household biogas digesters can be easily managed and operated without the need for complicated training for the users. A wider range of biomass can also be used as feedstock. Nonetheless, the anaerobic digestion process for the production of biogas involves complex interactions between diverse microorganisms and is discussed below.

3.1. Anaerobic digestion process

The anaerobic digestion process has four phases, namely, hydrolysis, acidogenesis, acetogenesis, and methanogenesis

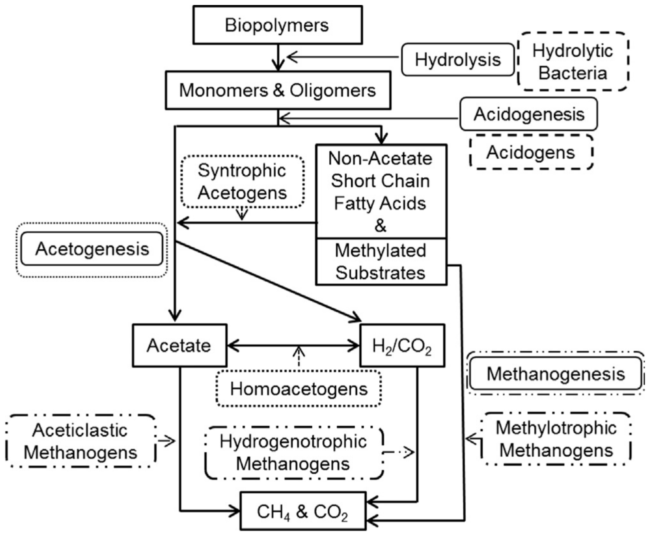

Fig. 2. The four phases of anaerobic digestion in biogas production showing the different organisms involved [60–64].

(Fig. 2) [61–64]. The hydrolysis, acidogenesis, and acetogenesis phases are collectively called the acidification step because of the drastic decrease in pH resulting from the fast occurrence of these phases compared with that of the methanogenesis phase [65]. The faster growth rate and lower physico-chemical sensitivity of the microorganisms in the acidification step commonly cause instability to the anaerobic digestion process.

3.1.1. Hydrolysis

In hydrolysis, strictly or facultatively anaerobic bacteria secrete extracellular enzymes that break down polymers of organic matter such as protein, polysaccharides, and lipids into their respective monomer and oligomer states. The anaerobic digestion of different biomasses completely depends on the capability of the microorganisms present as microflora or as microbial seed to produce appropriate hydrolytic enzymes for specific polymers. Amylolytic, proteolytic, cellulolytic, lipolytic, or phycocolloid-hydrolyzing bacteria can effectively hydrolyze starchy crops, protein-rich waste products, cellulosic plants, fatty fruits, or phycocolloid-abundant seaweeds biomass, respectively.

Lignocellulosic polymers are difficult to degrade; hence, pretreatment is needed to break down their complex structures and make cellulose accessible. Lignin cannot be degraded anaerobically because lignin-depolymerizing enzymes require oxygen. Before proceeding to acidogenesis, cellulose and hemicellulose, except lignin, are first digested by hydrolytic bacteria. Some microorganisms that can be found in an anaerobic digester include *Clostridia* species; this microorganism has cellulosome which is a multienzyme complex consisting of endo-1, 4-β-gluconase, exo-1, 4-β-gluconase, and β-galactosidase – that facilitates adhesion and complete hydrolysis of cellulose to glucose [66]. Hemicellulose such as xylan can be hydrolyzed into pentose sugar and xylose by some microbes such as *Caldicellulosiruptor saccharolyticus* [67].

3.1.2. Acidogenesis

Acidogenesis is the second phase in the anaerobic digestion process. The monomer and oligomer end products from the hydrolysis are instantly consumed in this phase by fermentative acidogens (strictly or facultatively anaerobic). Three major end-product substrates are produced in this phase and are grouped into (1) acetate, (2) hydrogen/carbon dioxide (H_2/CO_2), and (3) non-acetate short chain fatty acids, alcohols, and methylated substrates (NAM). Monomeric glucose from hydrolysis is converted into acetate, propionate, butyrate, ethanol [68], or methane with co-production of carbonic acid [62]. In the presence of xylose, H_2/CO_2 and acetate are produced by *Caldicellulosiruptor saccharolyticus* [67], among others, which simultaneously forms a syntrophic relationship with hydrogenotrophic methanogens [69].

3.1.3. Acetogenesis

The third phase, acetogenesis, is where the H_2/CO_2 and NAM substrates from acidogenesis are utilized by homoacetogens and syntrophic acetogens, respectively, for acetate conversion. Homoacetogens reduce CO_2 into acetate using H_2 as electron donor. In some cases, when population of aceticlastic methanogen, which consumes acetate in methanation step, is low, backward utilization of acetate substrate to produce H_2 and CO_2 is favored by homoacetogens in the presence of hydrogenotrophic methanogens. The latter simultaneously consume the H_2/CO_2 produced [64,70].

Moreover, the consumption of short chain fatty acids for acetate, CO_2, and H_2 production by syntrophic acetogens require an association with hydrogenotrophic methanogens. This syntrophic association allows immediate utilization of H_2 by hydrogenotrophic methanogen, lowering the H_2 partial pressure (< 10 Pa). The simultaneous consumption of H_2 permits the endergonic conversion of acetate and H_2/CO_2 by releasing the electron from NADH as molecular hydrogen, inducing forward reaction in this pathway [70].

Some acetogens such as *Syntrophomonas wolfei* and *Syntrophobacter wolinii*, which consume fatty acids and propionate, respectively, are in syntrophic relation with hydrogenotrophic methanogens [62,71,72]. On the other hand, propionate and alcohols are used by *Pelotomaculum* to produce acetate and H_2/CO_2 for the methanogenesis substrate [73]. Syntrophic acetogens such as *Acetobacterium woodii* [74], *Thermotoga lettingae* strain TMO [75], *Thermacetogenium phaeum* strain PB [76], and *Clostridium ultunense* strain B [77] are also associated with hydrogenotrophic methanogens [63].

3.1.4. Methanogenesis

There are three types of methanogens – (1) methylotrophic, (2) hydrogenotrophic and (3) aceticlastic methanogens – involved in the methanogenesis phase, which are classified based on the substrate they utilize. Methylotrophic methanogens consume the methylated substrates from the NAM that is produced during acidogenesis phase. Hydrogenotrophic methanogens utilize the H_2/CO_2 substrates that are the end-products of acidogens and homoacetogens and co-products of syntrophic acetogens. Aceticlastic methanogens use acetate substrates that are the end products in acidogenesis and homoacetogenesis and co-products in syntrophic acetogenesis [61,62,64,78]

Methanogens have six taxonomic orders (i.e., Methanococcales, Methanomicrobiales, Methanobacteriales Methanocellales, Methanopyrales, and Methanosarcinales) [79]. Four of these orders are commonly found in anaerobic digesters [80], namely, the hydrogenotrophic Methanococcales and Methanomicrobiales, which mostly use CO_2 and either formate or H_2 as electron donors; the hydrogenotrophic Methanobacteriales, which use mostly CO_2, and H_2 as an electron donor, but some use CO_2, and both H_2 and formate; and Methanosarcinales, which use acetate (aceticlastic), methanol and methylamines (methylotrophic), and H_2/CO_2 (hydrogenotrophic).

Two families under Methanosarcinales represent aceticlastic (Methanosaetaceae) and hydrogenotrophic (Methanosarcinaceae) methanogens in the anaerobic digester. Their dominance is dependent on the concentrations of short chain fatty acids and ammonia on the sludge. Methanosarcinaceae are predominant when concentrations of short chain fatty acids and ammonia in

sludge are high. Conversely, Methanosaetaceae predominates when these concentrations are low [81].

Methanogens appear to use H_2 more efficiently as shown by the low H_2 concentration, if not absent, in biogas, as compared to substantial amount of acetate substrate in the sludge after biogasification. Accordingly, enhanced CH_4 yield is observed in digesters added with hydrogen-producing bacterium *Caldicellulosyruptor saccharolyticus* [69]. The slow rate of acetate utilization compared with H_2 utilization during methanogenesis can be attributed to the slower growth rate of aceticlastic methanogens than hydrogenotrophic methanogens rather than the capacity to utilize the substrate itself. Hence, a more efficient utilization of H_2 than that of acetate may not be always true [62,69,78,82,83]. Biomass containing less protein that can be converted into ammonia during anaerobic digestion can be predominated by homoacetogens and hydrogenotrophic methanogens under thermophilic condition [81,84,85]. A possible shift to aceticlastic methanogens can be observed under mesophilic condition. Therefore, methanogen population dynamics can be influenced by several factors including substrate availability (acetate, short chain fatty acid, and ammonia) and operational conditions such as pH and temperature, among others [84].

In the sulfate-rich marine environment, sulfate-reducing bacteria (SRB) can outcompete hydrogenotrophic and aceticlastic methanogens because H_2S production is thermodynamically more favorable than CH_4 using short chain fatty acids, and H_2/CO_2. Hence, only methylotrophic methanogens are commonly observed in the marine environment because of the inability of SRB to utilize methylated substrates [86,87]. Upon sulfate depletion, SRB forms a syntrophic relationship with hydrogenotrophic methanogens, making H_2 as an electron sink and CH_4 as an end product [88].

4. Biomethane potential of seaweed biomass

4.1. Properties of seaweed biomass

Most seaweeds are composed of phycocolloids. *Kappaphycus alvarezii* (Doty) Doty ex Silva has high κ-carrageenan polysaccharide [89], where as *Eucheuma denticulatum* (Burman) Collins & Hervey contains ι-carrageenan [90]. *Sargassum* and *Padina* have 35% and 18.5% alginate, respectively [91]. Fucose and xylose are also present in *Sargassum* [92], whereas agar is the main component of *Gracilaria* [93]. In anaerobic digestion, the theoretical methane yield of a certain biomass can be obtained by determining elemental and proximate compositions. Different seaweeds contain different ratios of degradable components, which can significantly affect the efficiency of biogasification. Some important degradable components of the selected seaweeds *Sargassum* spp., *Turbinaria* spp., *Hydroclathrus* spp., *Caulerpa* spp., and *Ulva* spp. are discussed.

4.1.1. Elemental components

The elements in organic matter are mainly carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S). After moisture removal, the major compositions of biomass by mass are approximately 35–50% carbon and 40–45% oxygen [16]. The suggested optimum carbon to nitrogen ratio to achieve stable anaerobic digestion is between 25 and 30 [94]. A high amount of nitrogen is necessary for bacterial growth, especially during protein structure synthesis and nuclear matrix replication; however, an excessive amount may result in ammonia accumulation which has toxic

Table 3
The elemental compositions of the selected and other genus of seaweeds.

Species	Elemental composition (%, w/w dry)						Ref.
	C	H	O	N	S	C/N	
Selected Genus							
C. racemosa	38.03			2.06		18.45	[99]
				2.48		19.9	[100]
C. scalpelliformis	27.43			1.68		16.33	[99]
C. veravelensis	21.75			1.24		17.57	
H. clathratus					8.2		[101]
T. conoides						50.7	[102]
T. ornate				0.74		58.0	[100]
S. polyceratium	11.9			0.64		21.7	[103]
S. patens	40.18	5.22	33.85	2.00	0.98	20.09[a]	[104]
S. tenerrimum	22.44	4.34		1.83	6.60	12.26[a]	[105]
U. capensis				3.1			[106]
U. fasciata				1.44		25.7	[100]
U. lactuca				2.9			[106]
U. prolifera	29.7		50.1		2.97		[107]
U. lactuca (6 μM N)	37.0			1.66		26.02	[108]
U. lactuca (100 μM N)	38.13			4.09		10.88	
U. rigida				3.4			[106]
	28.7			1.3		22.1[a]	[109]
Ulva spp. (High N)				3.24		8.72	[110]
Ulva spp. (Low N)				0.88		30.71	
Other Genus							
Fucus serratus	33.5	4.78	34.44	2.39	1.31	14.02[a]	[111]
F. vesiculosus	32.88	4.77	35.63	2.53	2.44	13.00[a]	
Laminaria digitata	31.59	4.85	34.16	0.90	2.44	36.53[a]	
L. hyperborea	34.97	5.31	35.09	1.12	2.06	31.22[a]	
Macrocystis pyrifera	27.3	4.08	34.8	2.03	1.89	13.45[a]	

C – Carbon; H – Hydrogen; O – Oxygen; N – Nitrogen; S – Sulfur.

[a] Computed values by dividing N to C.

Table 4
The proximate compositions of the selected genus of seaweeds.

Species	Proximate values (%, w/w dry except moisture)						Ref.
	Lipids	CHO[a]	Protein	Fiber	Ash	Moisture	
Selected Genus							
C. lentillifera	0.86	59.27	12.49	3.17	24.21	25.31	[122]
	2.7	12.8	6.6		48.9		[123]
C. racemosa	19.1	83.2	18.3				[124]
	0.09	3.60	3.98	1.36	55.11		[125]
	3.8	16.6	6.8		42.2		[123]
	2.64	48.95	12.88		24.20	91.53	[99]
C. scalpelliformis	3.06	38.84	10.50		40.77	81.77	
C. veravelensis	2.80	37.23	7.77		33.70	87.88	
H. clathratus	2.18	82.26	6.39	2.70	6.47	59.63	[126]
	2.9	18.3	4.2		49.4		[123]
			8.6				[101]
S. decurrens	3.3	22.2	7.1		30.4		[123]
S. filifolium	4.0	21.4	10.2		28.2		
S. horneri	0.82	19.93	22.38		32.0	86.94	[127]
S. longifolium	8.2	16.8	18.65				[123]
S. mangarevense	3.4	24.9	13.2	17.9	60.6		[128]
S. naozhouense	1.06	47.73	11.20	4.83	35.18		[129]
S. patens					17.77	14.38	[104]
S. tenerrimum		8.20	0.86				[105]
	1.46	23.55	12.42				[130]
S. wightii	2.33	23.50	11–11.5				
Sargassum spp.	0.75	41.81	10.25	9.84	26.19	11.16	[58]
T. conoides	3.0	14.9	15.9				[131]
	1.9–2.1	23.9	11.5–12				[130]
	2.3	19.7	5.9		34.4		[123]
		31.83	8.6		34.30		[132]
T. ornata	2.2	24.6	9.2	13.5	39.8		[128]
T. triquetra	4.83	45.68	10.12		40.34	15.83	[133]
U. lactuca	1.6	23–24	3.25				[130]
	4.36	35.27	8.44				[134]
	1.64	14.6	7.06	55.4	21.3	10.6	[135]
U. reticulata	0.75	55.77	21.06	4.84	17.58	22.51	[122]
Ulva spp. (High N)		25.5	12.1	11.0			[110]
Ulva spp. (Low N)		51.4	3.6	4.3			

[a] CHO – Carbohydrates.

Table 5
The carbohydrate compositions (w/w dry) found on some of the selected genus of seaweeds.

Species	Compositions							Ref.
Brown seaweed	**% Cel**	**% He**	**% Alg**	**% Man**	**% Fu**	**% La**	**% Lig**	
H. clathratus			5.68	2.52		3.58		[136]
S. filipendula			14.4	0.8	26.0			[137]
S. ilicifolium				5				[138]
			30.80					[139]
S. muticum	2.2		16.9	7.7		0.3		[140]
S. tenerrimum				9.4				[138]
S. wightii			31.70	7.3				[141]
Sargassum spp.		25.73		5.04				[58]
T. conoides							19.27	[132]
				7.4				[142]
T. ornata			32.18	7.1				
T. triquetra			30.11					[133]
T. turbinata			24.6	0.2	32.1			[137]
Green seaweed	**% Cel**	**% He**	**% Rh**	**% Xy**	**% Ua**		**% Lig**	
U. lactuca	9.13	20.60					1.56	[143]
U. lactuca (Soluble fraction)			11.5	1.9	19			[114]

Cel – Cellulose; He – Hemicellulose; Alg – Alginic acid; Man – Mannitol; Fu – Fucoidan; La – Laminaran; Lig – Lignin; Rh – Rhamnose; Xy – Xylose; Ua – Uronic acid.

effects on methanogens [84,95,96]. Hence, the co-digestion of different biomasses are done to adjust the C/N ratio to an optimum value. The presence of a high amount of S as sulfate can also affect CH_4 production by encouraging the growth of SRB. These bacteria are more efficient in utilizing acetate and H_2/CO_2 substrates than aceticlastic and hydrogenotrophic methanogens, respectively [78,97]. This may cause the production of high amount of H_2S instead of CH_4, consequently decreasing biogas quality and combustibility.

Table 3 shows the elemental composition of the different selected seaweeds. Methane potential can be computed by using the elemental composition of the biomass through the formula of Buswell and Mueller [98]:

$$C_nH_aO_b+\left(n-\frac{a}{4}-\frac{b}{2}\right)H_2O\rightarrow\left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}\right)CO_2+\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)CH_4 \quad (1)$$

where n, a, and b are the mass fraction of elemental carbon, hydrogen and oxygen, respectively, on a dry weight basis of the biomass.

Computation of the theoretical methane yield using the elemental composition can overestimate the methane potential of a biomass because some amount of C, such as lignin, can be part of the non-degradable component of the biomass. Hence, proximate compositions are preferred for the methane potential computation of the biomass.

4.1.2. Proximate compositions

Table 4 shows the proximate compositions of the selected seaweeds. Fresh seaweed is mainly composed of moisture and total solid (TS, dry matter). Moisture content varies among seaweeds, ranging from 10% to 90%. Volatile solid (VS), which is computed by subtracting ash from TS, primarily affects the methane potential of seaweeds. Among the VS components, the carbohydrates, proteins, and lipids of the biomass are used to compute for the theoretical methane yield. The constant values of carbohydrate (fiber and N-free extract), protein, and lipid as suggested by Karpenstein-Machan [112 in 113] are 395 l CH_4/kg VS, 490 l CH_4/kg VS, and 850 l CH_4/kg VS, respectively.

Among the different carbohydrates components of the green seaweed *Ulva* (ulvan, α-cellulose, β-1,4-D-glucuronan and β-1,4-D-xyloglucan) [114–117], the sulfated ulvan can prevent the enzymatic digestion of α-cellulose [116,118,119], which may lead to incomplete hydrolysis. Brown seaweeds store carbohydrates as mannitol and laminarans, and their cell walls are composed of alginates and fucoidans [120,121]. Although most of the VS of seaweeds are mainly composed of carbohydrates, the structures differ with that of terrestrial plants, which are mainly composed of cellulose and starch. Hence, the ability of the microorganisms that are conventionally used in biogas fermentation to anaerobically degrade seaweeds may be limited. Table 5 presents the different carbohydrates found in seaweeds.

4.2. Methane fermentation of seaweed biomass

Many seaweed species have been studied as feedstock for methane fermentation. The theoretical methane yields of these seaweeds are high, but the actual methane yield of some species are low because of the presence of hydrolysis-resistant structural components or the absence of appropriate microorganisms that can breakdown the seaweed structures. Hence, the development of a suitable pretreatment for seaweed biomass is essential to maximize methane yield [144]. In the study of Bird et al. [2], *Sargassum fluitans* and *S. pteropleuron* yielded only 40% (450 l CH_4/kg VS) and 35.7% (420 l CH_4/kg VS) of their methane potential, respectively. Gupta et al. [145] discussed various approaches to enhance the methane yield of different biomass, such as co-digestion, as well as physical, chemical, and biological pretreatments. Physical pretreatment, specifically maceration, increases the methane yield of *Ulva lactuca* from 174 to 271 l CH_4/kg VS, whereas thermal treatment at 130 °C increases methane yield to 187 l CH_4/kg VS [146]. Without pretreatment, *Laminaria hyperborea* and *L. saccharina* produce 280 l CH_4/kg VS and 230 l CH_4/kg VS, respectively [147]. *Saccharina latissima* (*L.* saccharina) has low C/N ratio (8.8), but its methane yield (223 l CH_4/kg VS) is enhanced by 20.18% and 16.59% with a 10-min steam explosion pretreatment at 130 °C and 160 °C, respectively [148]. Moreover, the co-digestion of *S. latissima* with steam-exploded wheat straw (210 °C, 10 min) to increase the C/N value to 30.2 improves its methane yield to 270 l CH_4/kg VS [148].

The biomethane potential of *Ulva* sp. (196 l CH_4/kg VS), *Gracilaria* sp. (182 l CH_4/kg VS) and *Enteromorpha* sp. (154 l CH_4/kg VS) decreases (167, 170 and 148 l CH_4/kg VS, respectively) upon increasing TS input from 2.5% to 5% [149]. Furthermore, seaweed exhibit seasonal variation of methane yield. In *Laminaria digitata*, the highest actual methane yield (254.14 l CH_4/kg VS) is obtained on July and the lowest (196.33 l CH_4/kg VS) on March, corresponding to low and high ash content [150]. The seasonal variations in

the mannitol and laminaran content of *L. hyperborea* can also affect methane yield [151]. On the other hand, a two-day biological pretreatment of *L. japonica* (8.3 g Volatile Fatty Acid [VFA]/L), *Pachymeniopsis elliptica* (6.8 g VFA/L) and *Enteromorpha crinite* (4.4 g VFA/L) using *Vibrio harveyi* (15.6, 12.0 and 9.8 g VFA/L, respectively) and *V. alginolyticus* (~14, ~11.9 and ~7.5 g VFA/L, respectively) boosts VFA production, whereas chemical pretreatment using NaOH for 24 h is less effective (~12.8, ~9, and ~7.5 g VFA/L, respectively) [152].

The microflora of marine biomass can be used as microbial seed for anaerobic digestion [33], but operating conditions used in methane fermentation studies of seaweeds are patterned after biogas digesters running under terrestrial conditions (low salinity). Thus, the biogasification process utilizes washed biomass, freshwater liquid substrate, and conventional microbial inoculum. Operating conditions must be adapted to the requirements of marine microorganisms (thalassic), such as optimum salinity and temperature. With respect to anaerobic marine bacteria, *Clostridium halophilum* (degrades carbohydrates [78]), as well as *Halocella cellulotytica* [153 in 154] and *Sporohalobacter* [155 in 154] (both degrade cellulose), facilitates the anaerobic breakdown of cellulosic organic matter under high salinities. *Orenia marismortui*, *Halobacteroides halobius,* and *Sporohalobacter lortetii* metabolize glycogen and starch [156], and *Haloanaerobium praevalens* degrades pectin [154]. The presence of marine bacteria *Pseudoalteromonas citrea,* which degrades alginate [157], and *Pseudomonas galatica* [158] and *Vibrio* species, which can both metabolize agar [159] and alginate [152], may increase the anaerobic degradation treatability of the seaweeds.

The innate ability of marine bacteria to effectively digest the unique structural components of seaweeds may result in higher methane yield if these organisms are used instead of the conventional inoculum. Hence, digester operating conditions should be adjusted to the needs of the marine bacteria. Furthermore, the use of marine bacteria as microbial seed may minimize the pretreatment needs for seaweed biomass because marine bacteria are generally more efficient in degrading seaweeds than the terrestrial counterpart that has been gradually developed for thalassic conditions. Preliminary results of studies on the anaerobic degradability of *Ulva* spp. show higher methane yield under thalassic conditions using marine microbial inoculum than that under freshwater conditions, wherein conventional microbial inoculum that is primarily obtained from the continuous fixed-bed biogas reactor is used [160]. Thus, the potential of household digester operation in coastal community, together with the accessibility of seaweed as biomass feedstock and seawater as the liquid substrate, can be demonstrated under thalassic conditions. Coastal communities can greatly benefit from these conditions especially in terms of convenience in handling and managing digesters. Although different pretreatments can greatly increase the anaerobic degradability of seaweed biomass, most chemical and physical pretreatments are not accessible for island folks. However, biological hydrolytic pretreatment using facultative marine microbial inoculum may be the most suitable and cheapest way for utilization by island communities.

5. Engaging coastal communities on green energy

Coastal communities are often among the poorest of the poor, with little to no access to basic social services. These conditions increase their vulnerability to the risks and negative impacts of climate change, adding more challenge to an already difficult life. Poverty alleviation requires multi-faceted effort, and must harmonize the complex issues of human well-being with environment and ecological sustainability, among others.

Sustainability in energy production and utilization by coastal populations can be achieved by using renewable energy sources. The major considerations include accessibility and cost in acquisition. The capacity and availability of seaweed biomasses as feedstock for energy production are demonstrated herein. This information can be used for institutionalizing green energy production for coastal populations.

Different biogas digesters with varying capacities have been installed in some regions of the Philippines. There were 45 digesters ($\geq 500\ m^3$: 1; 100–499 m^3: 4; 10–29 m^3: 24; 1–9 m^3: 14; unknown: 2) in Region V: 25 digesters (all unknown capacities but were used for cooking/lighting) in Region IX: 13 digesters (30–99 m^3: 2; 10–29 m^3: 3; 1–9 m^3: 8) in Region X: 48 digesters ($\geq 500\ m^3$: 1; 10–29 m^3: 19; 1–9 m^3: 21; unknown: 7) in Region XI: and 15 digesters (10–29 m^3: 9; 1–9 m^3: 6) in Region XIII [161,162]. However, the biogas technologies that are widely used today utilize freshwater which is usually scarce in coastal areas, especially in island communities, where rainwater is often the primary source of freshwater. Thus, the rationalization of freshwater use is a must. Given that biogas technology under saline conditions is feasible [33], the use of seawater, which is abundant in these communities, is more practical.

Although biogas technology in the Philippines is already developed, operational digesters are few and biogas capacities are low because of the limited accessibility of the communities to the technology [163] and expensive investment cost of digesters [164]. The appreciation of biogas technologies remains low in the country, especially at the grass roots level. The dissemination of information on biogas technology, specifically an easily understandable yet complete technical know-how, to the local government units and communities are lacking. A more directed, intentional, and localized approach such as information campaigns using local dialects may go a long way.

Operational digesters can be demonstrated in the community, with emphasis on its convenience in utilization and its long-term cheaper cost than that of conventional fossil fuels. Government incentives on using green energy may also be institutionalized to encourage further green energy production and utilization, especially biogas technology. Engaging the private sectors through public-private partnerships may also improve the accessibility and prolific adoption of the technology. To augment the operational cost and further increase profitability, the utilization of digester waste sludge as biofertilizer for mariculture or agriculture can also be studied. If a commercial biogas plant is preferred to small digesters, sustainable and managed harvesting of natural stocks and extensive mariculture of seaweeds for feedstock demand can be done by coastal folks as a source of additional income. The utilization of these seaweeds as feedstock for biogas production must also consider the potential demands on the high-priced natural products derived from the aforementioned seaweed species (e.g., alginate and fucoidan from the brown algae *Sargassum*, *Turbinaria*, and *Hydroclathrus*), such that the utilization of these resources is maximized and the goals of sustainable development are achieved. Although seaweed biomass resources are the focus of this review, the potential of dislodged sea grass biomasses that are commonly mixed with seaweed must be also considered.

6. Conclusions

The managed exploitation of underutilized renewable resources is necessary to encourage and maintain sustainable growth. At present, much of the seaweed resources remain underutilized in many coastal areas of the Philippines and elsewhere in the world despite its great potential to support sustainable development. These resources also hold great potential as alternative sources of biofuel, especially for the well-being of coastal

populations. The major advantages of seaweeds over its terrestrial counterpart are its shorter life cycle and easier, more cost-effective, and often environment-friendly cultivation. Five of the most viable Philippine seaweed species are the brown seaweeds *Sargassum* spp., *Turbinaria* spp., and *Hydroclathrus* spp., and green seaweeds *Caulerpa* spp. and *Ulva* spp. *Sargassum* spp. is the most abundant and well-studied among the species. The presence of extensive *Sargassum* beds throughout the country led to the development of an ecologically-sound cropping management for the natural stocks. *Turbinaria* spp. has the second largest natural bed in the country, but studies on its ecology and distribution are still limited. However, it is believed that *Turbinaria* may be sustainably harvested using the management scheme developed for *Sargassum*. Although seasonal, the extensive blooms of *Hydroclathrus* and *Ulva* species are correlated with eutrophication and thus can be utilized as biomass source, which also serves as a potential pollution remediation. At present, only *Caulerpa* has an established culture technology in the Philippines among the species presented herein. Culture technologies for the other seaweed species should be developed to sustainably produce biomass as feedstock for biogas production and avoid adverse effects on natural stocks (e.g., species extinction). Thus, research and development on this aspect is wanting.

Seaweed biomass is often treated as terrestrial feedstock. Seaweeds are washed to remove salts and conventional microbial inocula are used to initiate anaerobic digestion. Although the methane yield in this route showed promising results, the required pretreatment under similar digester conditions may pose a great challenge to island communities because the required resources are often limited and not easily accessible (e.g., freshwater). Hence, the utilization of biogas technology for these specific users may not be appealing. Thalassic biogas digesters that are adapted to island communities and use the aforementioned seaweeds may provide cheaper alternative and environment-friendly energy source. Aside from the benefits received by coastal populations from the energy supplied by this green technology, the society also benefits from the reduced carbon footprint because of non-reliance to fossil fuels, therefore helping in mitigating the negative impacts of climate change.

Among the suggested seaweeds, only *Sargassum* spp. and *Ulva* spp. have been extensively studied as resource for biomethane production. Research on the anaerobic digestion of *Turbinaria* spp., *Hydroclathrus* spp., and *Caulerpa* spp. are still needed. The optimum operating conditions that are suitable for the Philippine climate and appropriate biomass pretreatment that can be handled easily need immediate investigation. The utilization of post fermentation residue as biofertilizer for agriculture and mariculture, especially in seaweed farming, also requires further evaluation because nutrient enrichment may cause microalgal blooms. In addition, the benefits of using commercial or household biogas digesters should be locally demonstrated to encourage further the utilization of biogas technology. Support from the government is essential in bridging the technology to the communities.

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